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ABSTRACT

Focused X-ray beams for the study of heterogeneous samples have proven to be an essential tool for many scientific areas from materials science to soft matter, chemistry and nanotechnology. By combining X-rays with Raman spectroscopy *in situ*, samples can be studied at several size scales simultaneously, from molecular vibrations to structure and form factors, with high resolution in real space. By using such combined techniques within a microfluidics device, reactions can be probed at different stages as the reactants mix and flow through the device. Here we present the first use of a microfluidics device in a combined μSAXS – μRaman study. The formation and growth of silver nanoparticles, and their functionalisation with cysteamine, was monitored. The combination of such techniques and sample environments open new opportunities for studying materials at the nanoscale.

Keywords: μSAXS, μRaman, microfluidics, silver nanoparticle, SERS

1 INTRODUCTION

X-ray techniques can provide a wide range of information from the sample under study. Wide angle X-ray scattering (WAXS) gives information regarding crystallinity, orientation and texture, whilst small angle scattering (SAXS) provides information regarding sample size, size distribution and shape. Both techniques have proven important for the study of nanomaterials.[1] Furthermore, by using focused X-rays, raster scanning of the sample provides detailed information; a reciprocal space image of the sample taken at every real-space coordinate, permitting a comprehensive study of a heterogeneous sample with real-space resolution limited by the beamsize. By combining X-ray techniques with Raman spectroscopy, samples can be probed at multiple size scales at the same time, from nanometre scale form and structure factors down to molecular orientation and vibrations, with a real-space resolution again being dependent on beamsize. The micro-Raman set-up at the ID13 beamline, ESRF, France, allows for combined Raman – X-ray studies *in situ* with a beamsize of ~ 1 μm^2.[2]

The field of micro- and now nano- fluidics has also seen tremendous development over the past few decades. The principal advantage being a significant reduction in required sample volumes.[3] However, microfluidic devices offer unique opportunities to study and manipulate mixing events, reactions and confined flow phenomena. By controlling flow rates and channel volumes, time resolution can be translated to spacial resolution which can be easily exploited using focused beams for X-ray and spectroscopic techniques. Due to a constant flow of material within the device radiation damage is no longer an issue, meaning acquisition times can be increased allowing for better signal/noise ratios whilst maintaining temporal resolution. Concentration profiles can also be easily studied by controlling flow rates.

Many studies combining microfluidic devices with focused beams for X-ray studies can be found in the literature,[4-8] as well as several studies using microfluidics with Raman spectroscopy,[9, 10] and more specifically, surface enhanced Raman spectroscopy (SERS). [11-15] Here, we present the first use of a microfluidics environment for combined μX-ray and μRaman studies. The formation of silver nanoparticles and their surface functionalisation with cysteamine has been observed. Indeed, the possibility of combining X-ray and Raman spectroscopy techniques in such an environment is particularly appealing to the study samples at the nanoscale, especially for the study of SERS substrates.

2 EXPERIMENTAL SET-UP

General procedures: All chemicals were purchased from Sigma-Aldrich and used without further purification. Water was purified using a Milli-Q purification system.

2.1 Microreactor

The microreactor used was based on a design previously developed for X-ray studies.[16] The reactor uses the tube-in-tube geometry.[17] The inner tube is made of 1/32 x 0.02 " PEEK tubing (Upchurch scientific). The outer tubing is made of a 1 x 1 x 100 mm borosilicate square capillary (VitroCom) thinned to a wall thickness of ~40 μm by etching with hot 40 % w/v NaOH solution. The square cross-section allows for a constant X-ray pathlength for

scanning laterally across the reactor channel. Solutions were injected using a Harvard PHD 2000 syringe pump at a rate of 0.1 mL.min^{-1}. The inner tube solution consisted of 400 mM $AgNO_3$ in H_2O. The outer tube consisted of a solution of cysteamine (400 mM) and NaBH4 (60 mM) in H_2O.

2.2 X-ray set-up

Experiments were performed at the ID13 microfocus beamline of the European Synchrotron Radiation Facility (ESRF). This beamline is optimised for micro- and nano-SAXS/WAXS and diffraction (XRD) experiments. X-ray data were recorded with a beamsize of 1.5 x 1.5 μm^2 at a sample-detector distance of 680 mm, providing a q range of 0.25 – 4.5 nm^{-1} using a wavelength (λ) of 0.8856 Å. SAXS patterns were recorded on a 16 bit readout FReLoN charged coupled device (CCD) detector with 2048 x 2048 pixels of 51 x 51 μm^2. Up to 10 x 30 s exposures were recorded at various positions in the microreactor channel (0 - 10 mm from the mixing point with 0.5 or 1 mm intervals). The corresponding background images (water) were collected prior to injection of the reactants. All images were corrected for the flat field and spatial distortion of the detector and normalised to the incident beam intensity. Background images were averaged and subtracted from the sample images. Normalisation, averaging and azimuthal integration were carried out using the *SAXSutilities* package (www.sztucki.de/SAXSutilities).[18] A hard sphere model from this package was used to fit the SAXS patterns.

2.3 *In situ* Raman probe

The *in situ* on-line fibre optic Raman probe was designed and built in collaboration with Renishaw © and has been described previously.[2] Briefly, the spectrometer is a research grade InVia Raman microscope from Renishaw©. The 785 nm near-IR excitation laser is coupled to the on-line probe via a 96 m long fibre optic cable, delivering a maximum of 130 mW on the sample focused to 1.1 μm^2. A 1200 lines mm^{-1} grating provides a spectral range of 600 cm^{-1} for single-shot (static) acquisitions. Raman acquisitions are triggered by the beamline control software allowing for simultaneous collection of Raman and X-ray data. 1 static exposure of 180 s centred at 800 cm^{-1} was taken at each position in the microreactor. Spectral acquisition, processing and curve fitting were carried out using the WiRE 2.9 software. A schematic diagram and photo of the experimental set-up can be seen in figure 1.

3 MONITORING NANOPARTICLE FORMATION AND GROWTH

3.1 Previous X-ray studies

Metallic nanoparticles are typically synthesised using standard “wet” chemical methods, by reducing a metal salt in the presence or absence of a capping agent.[19] The result being the formation of nanoscale metallic clusters, the size of which can be directed by the choice of reducing agent (citrate, sodium borohydrides etc), the ratio of capping agent / metal atoms, or indeed by controlling experimental conditions such as temperature, solvent etc. Typically, the reaction is very fast, taking only several hundredths of a second to completion. To study the formation mechanism would require a technique capable of measuring the size and size distribution of a statistically relevant quantity of particles with sufficient time resolution *in situ*. Several recent studies have used SAXS in a time resolved regime, or by using microfluidic devices in order to study these formation processes.[20-25]

3.2 Raman spectroscopy as a complimentary technique

Although the studies cited above give an excellent insight in to nanoparticle formation and growth, information regarding the physicochemical properties of the nanoparticles would give a more complete picture as they evolve from atomic-like clusters to particles exhibiting metallic character. For this, complimentary spectroscopic techniques are required. As the particles are SERS substrates, Raman spectroscopy is an obvious and attractive choice to compliment X-ray techniques. By choosing a suitable capping agent, its Raman spectra could be followed throughout the nanoparticle forming reaction. The intensity of the Raman bands would give an indication of the surface enhancement factor and, hence, metallic character of the particle, whilst a shift in the spectra would indicate changes in molecular vibrations resulting from binding to the particle surface. However, as Raman spectra typically require seconds, even minutes, to acquire, working in a time resolved regime would not be possible. Therefore a microfluidic device is required.

As a model system, we studied the formation and growth of silver nanoparticles and their functionalisation with cysteamine. Silver nanoparticles are well known as effective SERS substrates,[26] and cysteamine has a well characterised SERS spectra, exhibiting two binding conformations to metallic surfaces.[27, 28]

3.3 Results and discussion

From our experiments we were able to successfully observe silver nanoparticle formation within the

microreactor. The X-ray data indicate that nanoparticles form as the precursors mix, and that the particles grow as the reaction continues down the reactor channel. The smallest nanoparticle radius measured was ~0.5 nm, and after 3 s the nanoparticles appeared to stabilise at a radius of ~ 1.5 nm. The raman spectra indicate that cysteamine bound to the particle surfaces and that Raman band intensity increased with increasing particle size. Furthermore, a shift in wavenumber indicated a change in bond strength within the molecule as a function of particle size. Figure 2 shows a selection of SAXS curves obtained with their corresponding Raman spectra. Further details regarding experimental method, results and discussion will be presented in a future publication.

4 CONCLUSION

We have incorporated a microfluidics device in to the combined μX-ray – μRaman set-up of the ID13 beamline, ESRF. By combining μSAXS with μRaman spectroscopy, we were able to study nanoparticle formation and surface functionalisation within the microreactor channel. By combining X-ray and spectroscopic techniques in such a sample environment, physicochemical properties of growing particles can be monitored *in situ*. As the field of nanotechnology continues to grow, such combined techniques and sample environments will prove an important role for characterising the fundamental properties of such materials.

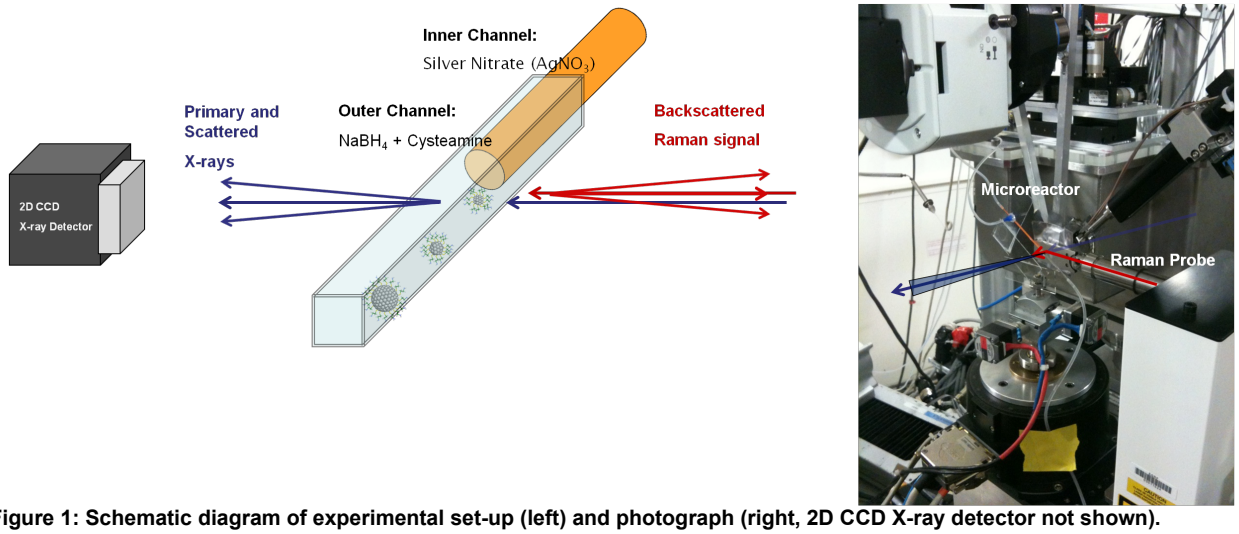

Figure 1: Schematic diagram of experimental set-up (left) and photograph (right, 2D CCD X-ray detector not shown).

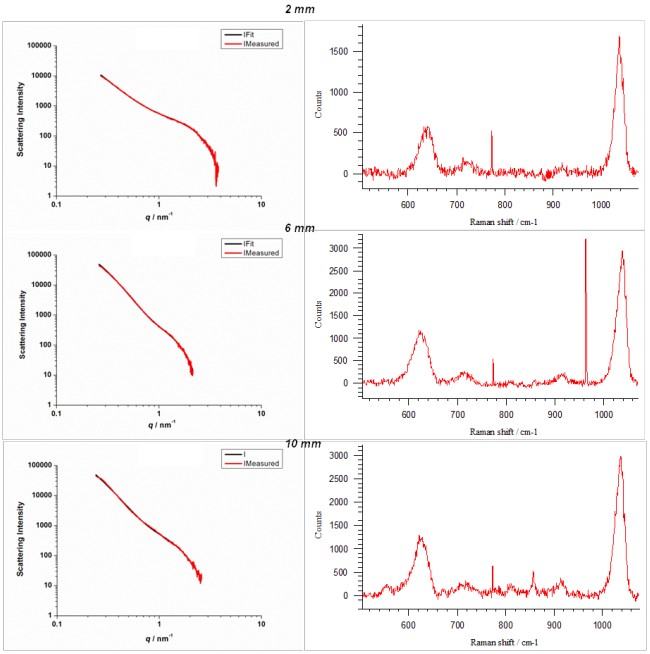

Figure 2: SAXS curves (left) and Raman spectra (right) at 2 mm (top), 6 mm(middle) and 10 mm (bottom) from the mixing point of the microreactor.

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